AFWAL-TR-82-4068
ADA119808

LOW COST AROMATIC ACETYLENE AND OLIGOMERIC BENZILS AND THEIR CONVERSION TO ACETYLENE TERMINATED QUINOXALINES.

E. T. SABOURIN

GULF RESEARCH & DEVELOPMENT COMPANY
P. O. DRAWER 2038
PITTSBURGH, PA 15230

July 1982

Final Report for Period 10 April 1981 to 30 March 1982

OFFICIAL FILE COPY

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Frederick L Hedberg

Frederick L. Hedberg, Contract Monitor
Polymer Branch

R. L. Van Deusen

R. L. Van Deusen, Chief
Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER

F. N. Cherry

Franklin D. Cherry, Chief
Nonmetallic Materials Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization, please notify AFWAL/MLBP, W-PAFB, OH 45433 to help us maintain a current mailing list".

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFWAL-TR-82-4068	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE *(and Subtitle)*: LOW COST AROMATIC ACETYLENE AND OLIGOMERIC BENZILS AND THEIR CONVERSION TO ACETYLENE TERMINATED QUINOXALINES.	5. TYPE OF REPORT & PERIOD COVERED: Final Report for Period 10 April 1981 to 31 March 1982
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): E. T. Sabourin	8. CONTRACT OR GRANT NUMBER(s): F33615-81-C-5016
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Gulf Research & Development Company, P. O. Drawer 2038, Pittsburgh, PA 15230	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: P.E. 61102F, Project 2303, Task 2303Q3, Work Unit 2303Q316
11. CONTROLLING OFFICE NAME AND ADDRESS: Materials Laboratory (AFWAL/MLBP), Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, OH 45433	12. REPORT DATE: July 1982
	13. NUMBER OF PAGES: 41
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*	15. SECURITY CLASS. *(of this report)*: UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Quinoxaline Oligomers
Bis(triphenylphosphine)palladium dichloride
4,4'-Bis(3-bromophenoxy)phenylsulfone

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A novel oligomeric acetylene terminated quinoxaline composition was prepared in a five step reaction sequence starting from m-dibromobenzene and acetylene. The new material showed a Tg of about 65°. Removal of catalytic amounts of palladium and copper used in the preparation was found to be very difficult. A 50 gram sample of the new resin was prepared and submitted to AFWAL/MLBP for evaluation. Research efforts to catalytically replace chlorine atoms in chloroaromatics by acetylene groups were unsuccessful. A study was made of the effect of temperature and pressure on the preparation of 4,4'-bis(3-bromophenoxyl)phenylsulfone.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

I. INTRODUCTION

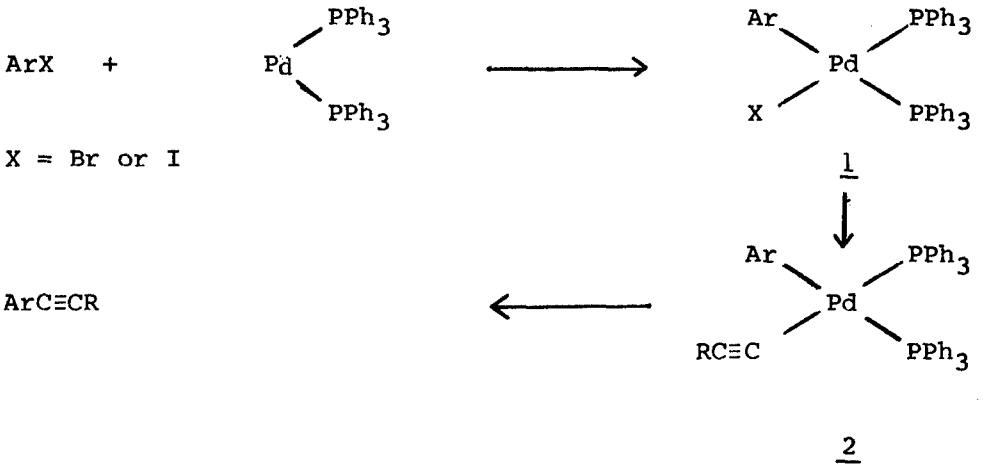
This report summarizes out work conducted from April 10, 1981, to March 31, 1982, on USAF Contract No. F33615-81-C-5016. The work involved three separate areas: a study of the feasibility of displacement of chlorine from chloroarenes with acetylenic groups by modification of the ligands on the catalyst, the preparation of oligomeric benzils and their conversion to acetylene-terminated quinoxalines, and a quick assessment of the effect of temperature and pressure on the preparation of 4,4'-bis(3-bromophenoxy)phenylsulfone.

II. LOW-COST AROMATIC ACETYLENES

A. Background

In recent years a variety of acetylene-terminated resins have been synthesized.[1,2] Introduction of the acetylene groups on a commercial scale by conventional methods such as the Vilsmeier reaction[1] or halogenation-dehalogenation of ketones[3] proved to be undependable and costly. The development of the methodology for displacement of bromine from bromoarenes with the commercially available protected acetylene 2-methyl-3-butyn-2-ol and the subsequent removal of the protecting groups has resulted in significant cost reduction in several cases.[4,5] Extension of this methodology to the chloroarene analogues would result in another order of magnitude cost reduction.

The proposed catalytic cycle for the displacement reaction is shown in Scheme 1. The poor reactivity of chloroarenes is most likely associated with their much slower rate of oxidative addition (Step 1, Scheme 1) than bromo- or iodoarene. Chloroarenes are known to react with tetrakis (triphenylphosphine) palladium at elevated temperatures to give the proposed intermediate 1.[6,7] Tetrakis (triethylphosphine) palladium is known to react at a much lower temperature to produce an analogous product.[8] It was hoped that modification of the ligand associated with the palladium would allow us to increase the rate of the acetylene displacement reaction.



Scheme 1: Proposed Mechanism for Catalytic Cycle

B. Preparation of Intermediates

Before proceeding with the ligand screening study, however, it was desirable to prove that intermediate 1 does indeed go to product. In our initial efforts to prepare 1, tetrakis (triphenylphosphine) palladium was refluxed in chlorobenzene for several hours since no experimental detail was indicated in the literature.[6] The only product isolated proved to be bis-(triphenylphosphine) palladium dichloride. The infrared spectrum was identical to authentic material (Strem). This indicated that 1 was probably carried on by a disproportionation to the ultimate product. Although all filtrates were examined by GLC for biphenyl, the most likely co-product, none was detected. In a second preparation

$$C_6H_5Cl + Pd[(C_6H_5)_3P]_4 \longrightarrow \begin{matrix} C_6H_5Pd[(C_6H_5)_3P]_2Cl + ((C_6H_5)_3P \\ \downarrow \\ Pd[(C_6H_5)_3P]_2Cl_2 \end{matrix}$$

the heat was removed immediately upon reaching reflux. In this case, the desired product and the disproportionation product were formed in roughly equal amounts. Fractional crystallization produced pure 1 mp 238-240°C (lit. 240°C).[6] Attempts to prepare 1 below reflux temperature led only to recovery of starting materials.

C. Use of the Substrate as the Solvent

Conversion of 1 to 4-phenyl-2-methyl-3-butyn-2-ol by warming with methylbutynol in the presence of cuprous iodide in triethylamine was very rapid, indicating that the acetylene can readily displace chlorine on palladium and that the reductive elimination is facile. This led us to believe that it might be possible to carry out the reaction using the chloroarene as solvent with a minimum of triethylamine to trap the HCl formed. Such a reaction was carried out at 128°C in a glass pressure vessel to keep the triethylamine and methylbutynol from distilling. No traces of product were found after 4 hr. A similar run using m-dichlorobenzene also gave no reaction. Since we know the oxidative addition is possible at this temperature, some

competing catalyst-deactivating reaction must be occurring with the other reagents at this temperature which apparently does not occur in the temperature range of 90 to 100°C. To ascertain if methylbutynol was the deactivating species, another run was made using trimethylsilylacetylene in place of the methylbutynol. Again, no trace of displacement was detected.

D. Ligand Screening Study

To screen as many catalysts as possible, it was decided to prepare the catalysts in situ from palladium acetate and the appropriate phosphine. This procedure is known to be effective for bromoarenes. In the early screening runs, 4-chlorobenzonitrile was the substrate because it is among the most reactive chloroarenes for oxidative addition.[7] Because we also wanted to test solvents other than triethylamine, some of which apparently reacts with the nitrile group, later runs employed 4-chlorobenzotrifluoride as the substrate. Standard temperature for the runs was 90°C (oil bath). Reactions were run for a minimum of 5 hr. In no case was more than a slight trace of displacement detected (GLC). A list of the ligands screened is shown in Table I.

In discussing this approach to the problem with Professor Richard Heck (University of Delaware), he indicated that he also had screened many phosphines, and the likelihood of success was very small. Dr. Heck reported that the palladium-catalyzed formate reduction of bromoarenes is usually stopped by the addition of chloroarene.[9] The nature of this deactivation is not clear. Since it has been shown that bromochlorarenes react readily with acetylenes to give selective displacement of the bromine, the same deactivation is probably not operative in this case.[10]

During the screening study, one unusual reaction was noted. In using diisopropylphenylphosphonite as the ligand, a facile head-to-tail dimerization of the 2-methyl-3-butyn-2-ol to give a 1,3-substituted enyne product in 90% selectivity. Some heavier material, probably trimer, was also produced.

$$2(CH_3)_2C(OH)C{\equiv}CH \longrightarrow (CH_3)_2C(OH)C{\equiv}C-\underset{\displaystyle C(OH)(CH_3)_2}{\underset{|}{C}}{=}CH_2$$

E. Conclusions

The conversion of bis-(triphenylphosphine) phenyl palladium chloride to 4-phenyl-2-methyl-3-butyn-2-ol under normal reaction conditions clearly shows that if oxidative addition to the chloroarene occurs, the conversion to product is facile. Since the reaction fails under conditions which are very similar to those for carrying out the oxidative addition (chlorobenzene solvent at reflux temperature), it appears that oxidative addition cannot compete with catalyst deactivation. Thermal decomposition of tetrakis (triphenylphosphine) palladium to palladium metal also occurs at about the same temperature. While ligand modification might lower the temperature at which oxidative addition occurs, the thermal stability of the palladium complex is also probably lowered. It is unlikely that any simple modification of the palladium phosphine catalyst system will effect the desired reaction.

III. PREPARATION OF OLIGOMERIC BENZILS AND THEIR CONVERSION TO ACETYLENE-TERMINATED QUINOXALINES

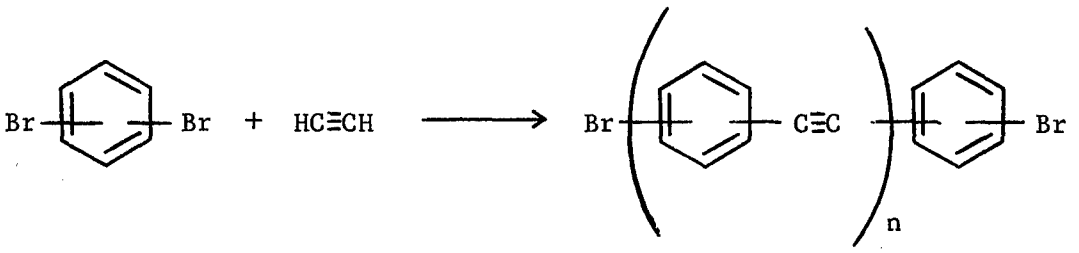
A. Background

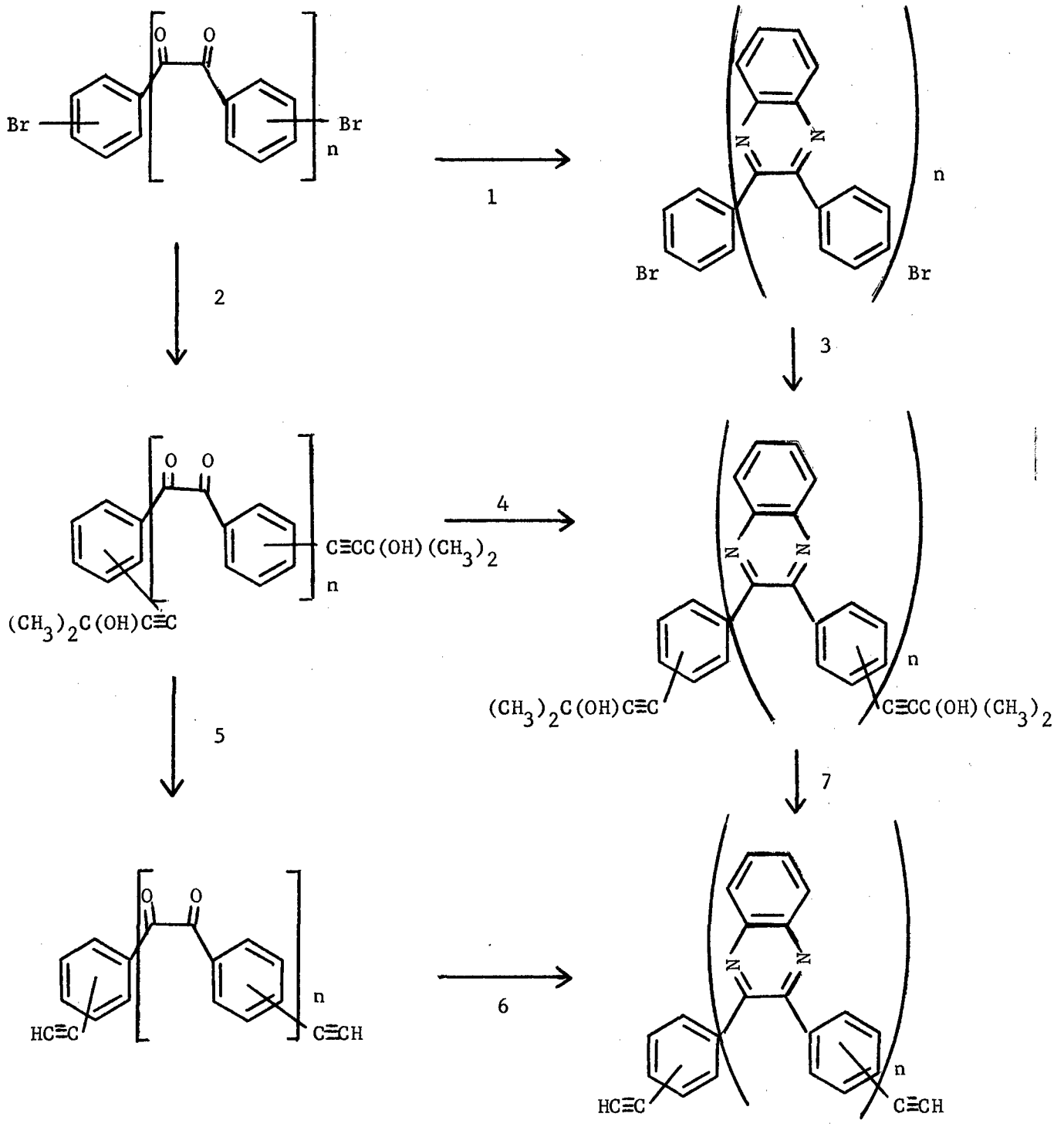
Recent studies on acetylene-terminated phenylquinoxaline oligomers (ATQ) have demonstrated significant improvements in processability compared to linear polyphenylquinoxalines due to their greater solubility in low-boiling organic solvents and high degree of flow at their softening temperature.[1] Despite the improvement, the softening point of most of the ATQ's remains too high for neat processing. The use of reactive diluents offers some help, but a change in overall oligomer structure which lowers the softening point would be of more value. One reason for the higher-than-desired softening points may be the high degree of symmetry in the ATQ's. This in turn is due to the fact that only symmetrical bis-benzils and tetra-amines are available. Availability of more asymmetrical polybenzils might alleviate the problem and also allow the use of cheaper, more readily available, less carcinogenic diamines.

Direct condensation of acetylene with dibromoarenes had been shown to lead to mixture of bromo-terminated oligomeric arylacetylene polymers.[11] If this process could be optimized and the resulting oligomers oxidized to the analogous benzils, conversion to ATQ oligomers might be attainable via the routes depicted in Scheme 2. The possibility of controlling the orientation of the oligomers by varying the m,p ratio of the dibromoarene combined with the use of mixtures of oligomers of different molecular weight offered considerable hope of producing readily processable materials.

B. Preparation of Oligomeric Arylacetylenes

The preparation of bromine-terminated arylacetylene oligomers is depicted below.





Scheme 2. Possible Synthetic Sequences to ATQ

The greater reactivity of arylacetylenes compared to acetylene itself leads to almost exclusive bromine end groups. Previous work suffered from very slow reaction rates when using standard conditions of other bromine displacement, e.g., triethylamine solvent and bis-(triphenylphosphine) palladium dichloride catalyst.[11] Initial attempts to improve rates by varying catalyst and solvent are shown in Table II. Run 7 demonstrates little improvement in employing tolylphosphine ligands on the catalyst. Switching to a higher boiling amine solvent, dipropylamine, showed an improved rate, but the product was very insoluble and settled out during reaction. This caused difficulties in stirring, poor heat transfer, and extensive crosslinking, Run 9. Use of a larger ratio of dibromobenzene to solvent raised the reflux temperature and improved the solubility of the product, but it is impossible to generate significant amounts of material with higher values of n in this manner. Replacing a portion of the amine with a variety of dipolar solvents showed significant improvement. Dimethylsulfoxide appeared to be the best cosolvent, but even there the product comes out of solution in the latter stages of the reaction. Attempts to use cosolvents in which the product is very soluble, e.g., chlorobenzene, were frustrated by exceedingly slow rates. The use of diisopropylamine in combination with the dimethylsulfoxide gave a system which was readily controlled at 93-94°C by reflux. Lower temperature gave slower rates. Triethylamine or dipropylamine tended to give mixtures which refluxed at temperatures above 115°C where catalyst stability is not as great.

It was felt that the dimethylsulfoxide diisopropylamine solvent system was adequate to begin some small-scale preparative runs. Table III summarizes a number of runs designed primarily to generate material to check out the remaining steps in the sequence. Modifications of the reaction procedure were slight. In the displacement of heavy bromine atoms by light acetylene molecules, as the degree of oligomerization goes up, the theoretical weight of oligomer goes down. This means that the actual weights of product are not of paramount significance. The only convenient monitor of the system was the disappearance of dibromobenzene. This was generally monitored by GLC, but samples were taken no more than once an hour, so the times indicated are

only approximate. In any event, while general reproducibility is good, exact reproducibility is impossible. Nevertheless, some information can be gained from the data.

The presence of excess phosphine has been shown to stabilize the catalyst but generally causes decreased rates by blocking coordination sites.[4,12] The loss of phosphine by conversion to phosphonium salts is evidently quite rapid for the dibromobenzene reactions. Increasing the ratio of phosphine to palladium from 5.3/1 to 8.6/1 actually caused a significant rate increase in Runs 75, 114, and 115.

The presence of cuprous iodide shows little effect in the reaction of bromoarenes with olefins.[9] The effect in the acetylene reaction, however, is very significant. Cuprous iodide probably is involved in two modes. Sonagshira postulated the function of cuprous iodide as the reduction of divalent palladium to zero-valent palladium.[13] Cuprous iodide will also give a significant rate enhancement even when the starting catalyst is zero-valent palladium.[11] This can be interpreted as catalysis of the displacement of halogen from palladium prior to the reductive elimination.

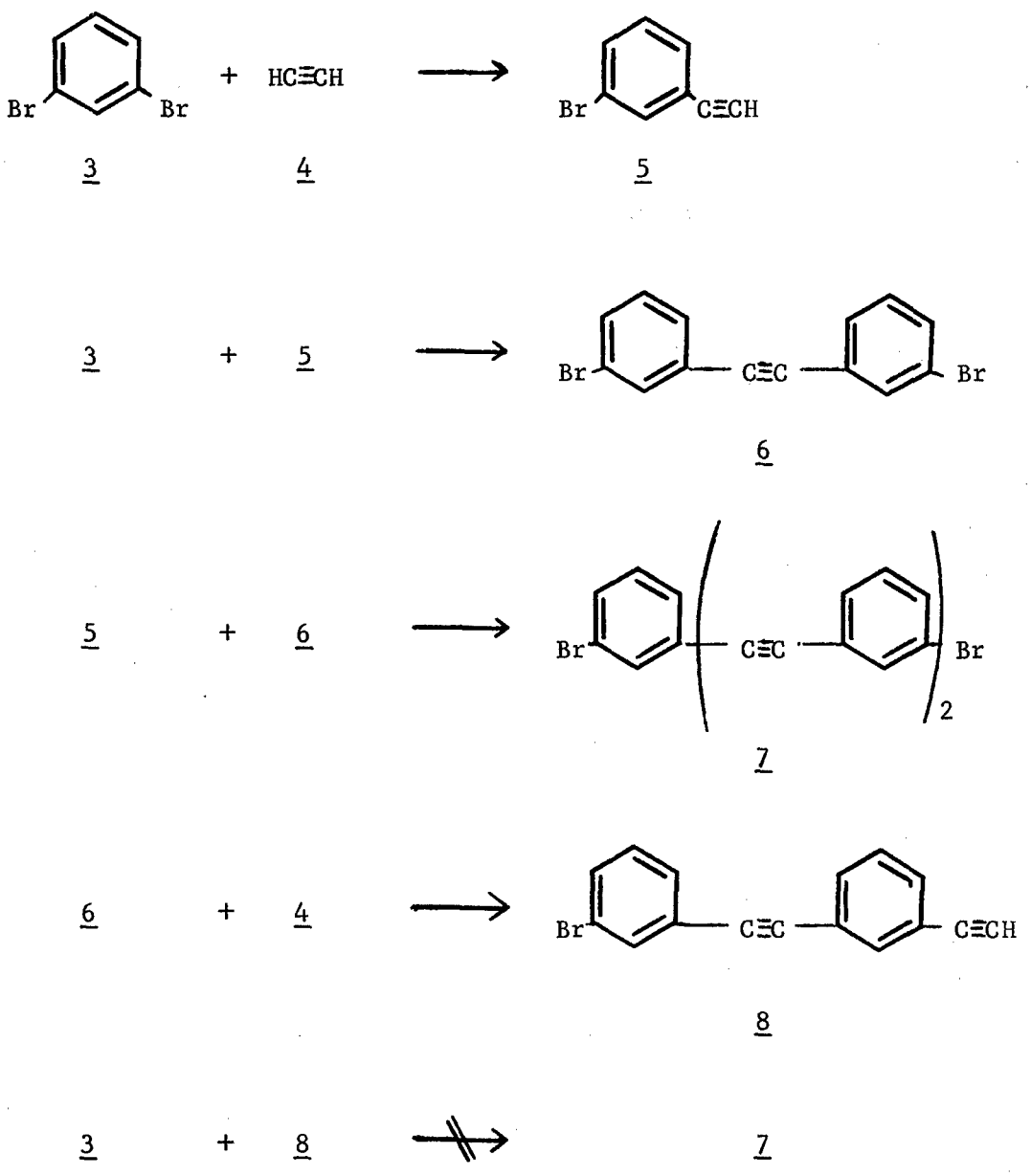
$$ArPdL_2X + HC{\equiv}CR \xrightarrow{CuI} ArPdL_2C{\equiv}CR + HX$$

One of the major problems associated with this oligomerization is a side reaction which produces a material which is insoluble in dichloromethane, an excellent solvent for the desired oligomers. This material is thought to be a crosslinked polymer. The amount of polymer present was not routinely measured since it is readily removed in subsequent steps. However, sufficient determinations were made to indicate that the problem occurs when trying to attain higher values of n. For example, early runs in which excess dibromobenzene remained showed no insolubles. Those runs terminated shortly after the dibromobenzene was consumed showed 10-15% insolubles or 712-30,45. Running the reaction for extensive time after the dibromobenzene was gone resulted in completely insoluble product--723-67. Some loss to polymer could

probably be tolerated if a sufficient improvement in the value of n could be attained. Table IV summarizes some analyses of the oligomer distribution made by HPLC on a number of samples. As long as dibromobenzene remains, no significant amount of n=3 or higher occurs. Longer reaction times, however, increase n much too slowly to compensate for the losses to crosslinked polymer. Addition of a second charge of dibromobenzene after the first was nearly consumed had no significant effect on the distribution--752-1.

An alternative method of improving the value of n is to extract the lower oligomers from the mixture. Warm hexane was found to be suitable for removing most of the n=1 material and some of the n=2 fraction. Table V shows the HPLC analyses before and after extraction.

The reaction of n=1 and 2 material from the extractions with acetylene or diethynylbenzene could cause n to increase in jumps of two or three units at a time. Unfortunately, attempts to accomplish this resulted in almost completely insoluble product. Furthermore, if samples are taken early in the reaction, the methylene chloride soluble portion continues to look like the starting material. This seems to indicate that arylacetylenes containing another acetylene substituent, such as 8 in Scheme 3, in the meta position have an even greater tendency to form insoluble crosslinked materials than the originally formed m-bromophenylacetylene. To check this out, m-bromophenylacetylene was reacted with lower oligomers by dropwise addition over several hours. The results of two such experiments are summarized in Table VI. A buildup in the higher oligomers is definitely shown, indicating that the bulk of oligomer growth occurs one unit at a time. The competing polymerization reaction is not restricted to those materials containing terminal acetylenes since the total dichloromethane soluble portion is less than the starting material.



Scheme 3. Reaction of Dibromobenzene with Acetylene

Attempts to react diethynylbenzene with dibromobenzene usually resulted in mostly insoluble material. However, dropwise addition did result in a modest yield of n=2 material containing traces of n=4. Use of zero-valent catalyst at lower temperature (70°C) did give a low yield of n=2, 4, 6, and 8.

Attempts to react 4,4'-dibromodiphenyl ether with acetylene gave even poorer results than dibromobenzene. This is undoubtedly due to the deactivation by the ether linkage.

C. Conversion to Oligomeric Benzils

A number of reagents have been reported to give high yields of benzils from diarylacetylenes including potassium permanganate,[14] N-bromo-succinimide in dimethylsulfoxide[15] potassium chlorate with osmium tetroxide catalyst,[16] and periodic acid.[17] In each case, a competing reaction is the cleavage or rearrangement of the benzil to carboxylic acids. It was expected that the multiple acetylenic groups in our oligomers would lead to larger inefficiencies based solely on statistics. These expectations were fulfilled.

Initial efforts employing phase transfer conditions are summarized in Table VII. Adogen-464 is an effective transfer agent; however, a relatively large amount is required.[14] This leads to problems in removing it from the oligomeric mixtures obtained in this case. Use of a crown ether is slow and erratic. Failure to react at all in several cases may be due to solubility of the particular batch of oligomer used or to completely anhydrous conditions. Small amounts of acetic acid seem to help the reaction. The yellow products isolated all exhibited strong carbonyl absorption in the IR at 1675 cm^{-1}. However, ^{13}C NMR showed significant amounts of acetylenic carbon still present. Insensitivity to temperature and the amount of permanganate indicated a problem after initial reaction. In one run, the brown precipitate which forms was filtered. The solvent was colorless. Evaporation showed only traces of residue. Treatment of the filter cake to the usual reductive work-up produced the usual product. Evidently the partially oxidized material is

strongly adsorbed on the manganese dioxide or, more likely, the brown solid is an organomanganese intermediate which is very insoluble. Therefore, this approach was abandoned.

Attempts to find a solvent which could dissolve both the oligomer and the potassium permanganate to give a homogeneous system are summarized in Table VIII. Tetrahydrofuran was shown to react with permanganate in a blank run at a rate which was competitive with the oxidation of the oligomer. Dimethylacetamine exhibited good reactivity. However, the cleavage of the longer chains is very high. The product in all runs was mostly n=1 benzil even though only 22% n=1 material was present in the starting oligomer. Acetonitrile gave similar results.

Buffered aqueous-acetone systems as per Lee[18] are not efficient principally due to the poor solubility of the oligomer in acetone. However, we did find that the addition of dichloromethane improved the system. A rather complex solvent mixture consisting of dichloromethane, acetone, acetic acid, and water in the approximate ratio 6, 2, 1, and 1 seemed to offer the best combination of solubility of all reactants for this reaction. The variations in the oligomer mixtures, particularly insolubles content, make the yields and the amount of permanganate required very difficult to judge. Table IX summarizes the results obtained in mixed solvent systems.

The oxidation does result in the reduction of the average n of the oligomers. This is illustrated for several typical runs in Table X. This reduction in n would undoubtedly be worse if higher overall values were attainable in the early steps. Attempts were made to offset the loss slightly by extraction of the lower benzil oligomerization with isopropanol, Table XI. The effect here is not as great as in extraction of the acetylene oligomers.

Attempts to use periodic acid for the oxidation gave partial oxidation. The product was contaminated with an enol-acetate species.

D. Conversion of Oligomeric Benzil to Acetylene-Terminated Quinoxalines

Conversion of the bromine-terminated benzils to ATQ's involves three steps. Several possible sequences are shown in Scheme 2. Preliminary experiments established that either route 1, 3, 7 or 2, 4, 7 produced the desired materials with the former appearing somewhat cleaner. The route involving 5 was subject to benzilic acid rearrangement and was therefore eliminated from consideration.

Reaction of oligomeric benzils with o-phenylene-diamine was accomplished in refluxing toluene with azeotropic removal of water. The product was isolated by precipitation in methanol. Only moderate yields, 50-80%, were attained because of slight solubility of the product. Second crops were always contaminated with the excess o-phenylenediamine.

The amount of water formed serves as another method of determining the value of n. In early samples where n was about 2, agreement between HPLC, bromine analysis, and water formation were in close agreement--usually ±0.2 units. Upon pushing for higher value of n, larger deviations occurred. Nitrogen analysis was usually slightly lower than expected, also. IR indicated no residual carbonyl groups so reaction of the benzils was complete. These difficulties in finding accurate methods of analysis are another of the major difficulties in the process.

Conversion of the bromoquinoxalines oligomers to the methylbutylnol derivatives is accomplished readily in triethylamine solvent using bis-(triphenylphosphine) palladium dichloride and cuprous iodide catalysts. The reaction can be monitored by HPLC. Surprisingly, the product is very soluble in methanol, and initial isolation is best accomplished by precipitation in hexane. Removal of the metal catalysts at this point is necessary to prevent premature curing of the final resin. In the case of acetylene-terminated sulfones, the removal was accomplished by treatment with ethylene-diamine and extraction of the resulting complex.[5] Unfortunately, the quinoxaline nucleus evidently holds onto metals much more tenaciously. Table XII lists a number of methods employed to remove the metals. None were completely

effective. Repetition usually provided only minimal improvement. Palladium levels of about 40-50 ppm and copper levels of about 10 ppm will allow cleavage of the acetone-protecting group and isolation of the product. DSC on the resulting products indicates that the onset of curing occurs at about 150-160°C with a maximum being attained at 225-250°C. No obvious melting point could be detected with DSC even with n=2 material (712-70) which in a melting point tube showed that the material began to pull away from the walls at 70°C, was completely translucent at 90°C, and slowly flowed to the bottom of the tube at 115°C. Unfortunately, as the value of n was increased, the melting temperature also increased. A sample of n=4 prepared by extracting lower ATQ oligomers with methanol showed no liquid phase until about 150°C, which is so close to the onset of curing that only a very small processing window would be available.

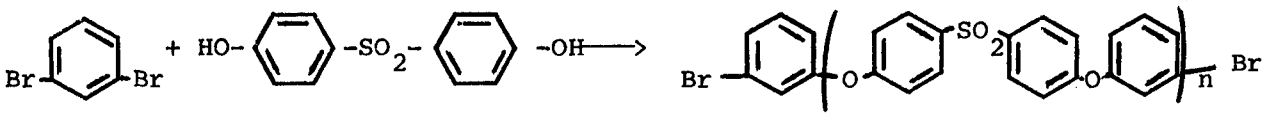
E. Conclusions

The preparation of several samples of ATQ oligomers by a novel route has been demonstrated. Significant improvement in the rate of reaction of acetylene with dibromobenzene has been achieved. However, production of significant amounts of oligomers with n greater than 3 cannot be accomplished without excessive losses to insoluble crosslinked polymer. Furthermore, if higher values of n could be attained in the initial oligomerization, much of the gain would be lost in the oxidation step since the higher oligomers are more readily cleaved to acid by-products. The extreme difficulty in removing the lost traces of catalyst metals from the product results in a lowering of the curing temperature which will lead to processing difficulties. Even if the samples provided have excellent properties, it is unlikely that economical production is possible by this route.

IV. EFFECT OF TEMPERATURE AND PRESSURE ON THE PREPARATION OF BIS-4,4'-(3-BROMOPHENOXY) DIPHENYL SULFONE (BPDS)

A. Background

In the preparation of acetylene-terminated sulfone resins (ATS), the first step is the condensation of dibromobenzene (DBB) with sulfonyldiphenol (SDP) to give a mixture of DPDS and higher oligomers.[5,19]



The previously developed procedure did not allow the preparation of material with very high oligomers content which was desired to reduce brittleness.[20] A new modified procedure developed at AFWAL/MLB employing cuprous oxide and collidine catalysts has proven effective in giving precise control of oligomer content at moderate DBB/SDP ratios. However, in order to obtain very high oligomer content, ratios of 6:1 or less are required. The viscosity of the mixture under these conditions made it difficult to attain complete conversion even at extended reaction times. The Project Officer requested that the effect of higher temperatures attainable by running the reaction under pressure be examined briefly to determine the feasibility of operation.

B. Results and Discussion

A control experimental run at reflux and atmospheric pressure was monitored by TLC. Complete disappearance of SDP occurred in about 44° hr. The remaining reactions were run in a magnetically stirred glass reactor which had no sample port. Therefore, arbitrary reaction times were chosen which did not always give complete conversion. However, it is clear from the entries in Table XIII that this mode of operation can significantly reduce the time requirement. No detrimental side reactions were noticed at temperatures up to 210°C. Improvement in agitation by going to a mechanical stirrer should result in further improvement. The crude products were analyzed by column

chromatography and HPLC. The results were in fair agreement. It is of interest to note that the ammonia wash used in the work-up procedure did not remove the half-product from the mixture. When considering recycle, this might allow separation of SDP from half-product by sequential ammonia and sodium hydroxide washes.

C. Conclusion

Higher reaction temperatures attainable by operating under pressure give significantly improved reaction rates for BPDS and oligomer production with no detrimental side reactions. This mode of operation could alow the use of cheaper, less noxious amines than collidine. The major concern would probably be abrasion of the glass reactor if the cuprous oxide level is not lowered.

V. EXPERIMENTAL

A. Reaction of Tetrakis-(triphenylphosphine) Palladium With Refluxing Chlorobenzene (712-1)

A mixture of 4.4_2 $Pd(PPh_8)_4$ and 50 mℓ chlorobenzene was refluxed under nitrogen for 5 hr. The mixture was cooled to room temperature and filtered. The yellow solid was washed with ether. A total 2.90 g of product was obtained, mp 280°C (dec). The infrared spectrum was superimposable with an authentic sample of bis-(triphenylphosphine) palladium dichloride. The filtrate was examined by GLC, but no biphenyl could be detected.

B. Preparation of Bis-(triphenylphosphine) Phenyl Palladium Chloride (712-2)

A mixture of 3.0 g $Pd(PPh_3)_4$ and 50 mℓ chlorobenzene was warmed in a nitrogen atmosphere. The wine-red mixture changed to a clear yellow upon reaching reflux, 129°C. The heating mantle was removed and the mixture allowed to cool to room temperature. Filtration produced 0.8 g bis-(triphenylphosphine) palladium dichloride. The filtrate was stripped in vacuo and the residue extracted with benzene, 30 mℓ. Addition of methanol precipitated the desired product as a white solid, mp 235-7°C (dec), 0.95 g. Recrystallization from xylene-hexane raised the mp to 239-240°C (lit. 240°C).[6]

C. Reaction of Bis-Triphenylphosphine Phenyl Palladium Chloride with Methylbutynol (712-3)

A three-necked flask was charged with bis-triphenylphosphine phenyl palladium chloride, 0.30 g; 2-methyl-3-butyn-2-ol, 2 mℓ; triethylamine, 5 mℓ; and cuprous iodide, 0.01 g; and placed under nitrogen. Upon warming to 75°C the mixture turned red-brown. Gas chromatography indicates the presence of 2-methyl-4-phenyl-3-butyn-2-ol (spiked with authentic sample).

D. Attempted Methylbutynylation of Chlorobenzene in Chlorobenzene Solvent

A magnetically stirred glass pressure vessel was charged with 2-methyl-3-butyl-2-ol, 10 g; triethylamine, 15 mℓ; triphenylphosphine, 0.5 g; bis-(triphenylphosphine) palladium dichloride, 50 mℓ; and cuprous iodide, 50 mg. The system was purged with nitrogen by pressuring to 50 psig and depressuring four times. The mixture was heated to 130°C for 4 hr. GLC showed no trace reactions.

A similar reaction with m-dichlorobenzene also failed. A similar reaction employing trimethylsilylacetylene in place of the methylbutynol also failed.

E. Ligand Screening Procedure

To a 100 mℓ flask equipped with a magnetic stirrer, condenser, nitrogen inlet-outlet, and a rubber septum sample port was added 20 mmol of substrate (either 4-chlorobenzonitrile or 4-chlorobenzotrifluoride), 24 mmol (2.00 g) 2-methyl-3-butyn-3-ol, 0.1 mmol (0.023 g) palladium acetate, 0.4 mmol of the ligand to be screened, and 25 mℓ of triethylamine. A nitrogen atmosphere was established. Cuprous iodide, 0.5 mmol, was added and the flask immersed in an oil bath maintained at 90°C. Samples were withdrawn periodically and examined by GLC. Table I lists the ligands screened.

F. Dimerization of 2-Methyl-3-butyn-2-ol (725-49)

When the above screening procedure employed diisophophlphenylphosphonite as the ligand, GLC revealed a facile dimerization of the acetylene component. The solvent was stripped and the residue triturated with hexane to produce a tan solid, 1.5 g, mp 69-74°C. Recrystallization from cyclohexane raised the mp to 77.5-79°C. NMR ($COCl_3$) δ 1.40(s,6H), 1.55(s,6H), 2.6(bs,2H, exchanges with D_2O), 5.30(d,J=2,1H), 5.45(d,J=2,1H).

G. Reaction of Dibromobenzene with Acetylene - General Procedure

A 1-ℓ flask equipped with heating mantle, condenser, thermocouple, magnetic stirrer, nitrogen inlet-outlet, and an acetylene delivery system was charged with m-bibromobenzene, solvent, phosphine, palladium catalyst, and cuprous iodide. The system was purged with nitrogen and heated to the desired temperature. Acetylene was bubbled into the bottom of the flask through two sulfuric acid scrubbers and an ice trap. It is necessary to use an unrestricted glass tube rather than a frit because solids can build up at the point of entry. A mercury bubbler relief device was hooked into the feed system in case a blockage did occur. The reactions were monitored periodically by GLC to check for the presence of DBB. Reaction mixtures which still contained DBB were worked up by stripping solvent, dissolving the residue in dichloromethane or toluene, washing with dilute HCl and water to remove traces of amine and salts, drying over magnesium sulfate, and vacuum distillation of DBB to give the product as the pot residue. Products for those reactions in Table III were obtained by slowly adding the entire reaction mixture to several liters of water with vigorous agitation. The tan precipitate was filtered and washed thoroughly with water followed by vacuum drying at 60°C to constant weight. The products typically began to melt at about 75°C. NMR shows no evidence for -C≡CH, only complex aromatic multiplet from 6.9-78.8 δ.

H. Determination of Insolubles

Oligomer (5.00 g) and dichloromethane (100 mℓ) were stirred vigorously for 30 min at ambient temperature. Filtration through a tared medium porosity glass filter and washing with about 25-mℓ dichloromethane produced solid which was dried in place and weighed.

I. Determination of Oligomer Distribution

HPLC determination of the oligomer composition at each step of the synthesis could be carried out on a 25-cm bonded phase nitrile column by varying the solvent composition. Flow rates were usually 2 mℓ/min. In the absence of pure standards, response factors were assumed to be unity. Average

values of n as determined by HPLC usually agreed with values determined by bromine analysis within ±0.2 units. The solvent composition used for each type of oligomer is shown below:

Oligomer Type		Solvent, Volume Percent		
Function	End-Group	Hexane	Dichloromethane	Isopropanol
Acetylene	Bromine	96.9	3.0	0.1
Benzil	Bromine	75.0	24.5	0.5
Quinoxaline	Bromine	75.0	24.5	0.5
Quinoxaline	Methylbutynol	49.0	50.0	1.0
Quinoxaline	Acetylene	84.7	15.0	0.3

J. Extraction of Lower Oligomers from Bromine-Terminated Phenylacetylene Oligomers (752-7)

The following run is illustrative of the general procedure. The combined products from the palladium-catalyzed reaction of acetylene with m-dibromobenzene from Runs 752-3, -4, and -5 (124.9 g) were slurried with hexane (1-ℓ). The magnetically stirred mixture was warmed to about 50°C for 1 hr. Upon cooling to ambient temperature, the mixture was filtered. The filter cake was vacuum dried to give 99.9 g of tan powder $\bar{n}$=3.4. HPLC analyses of the initial and final materials are shown in Table V.

K. Reaction of Bromophenylacetylene with Lower Bromine-Terminated Phenylacetylene Oligomers

A 500 mℓ flask equipped with a magnetic stirrer, heating mantle, condenser, thermocouple, nitrogen inlet-outlet, and an additional funnel were charged with oligomer (10 g), diisopropylamine (100 mℓ), dimethylsulfoxide (200 mℓ), bis-triphenylphosphine palladium dichloride (0.4 g), triphenylphosphine (0.5 g), and cuprous iodide (0.2 g). The system was purged with nitrogen and the mixture was brought to gentle reflux, ca. 90°C, and bromophenylacetylene (10 g) was added via the additional funnel over a 2-hr period. The precipitate was filtered and washed thoroughly with water then dried in a vacuum oven at 50°C to give 15.89 g tan solids. This product was slurried

with dichloroethane for 20 min and filtered to give 9.48 g of insolubles after drying. The analysis of the soluble portion is shown in Table I.

A second run employed 20 g of bromophenylacetylene added over a 4-hr period. Pertinent data appear in Table VI.

L. Reaction of Dibromobenzene with Diethynylbenzene (712-8)

A 500 mℓ flask equipped with magnetic stirrer, heating mantle, condenser, thermocouple, and nitrogen inlet-outlet was charged with 46.8 g m-dibromobenzene, 12.6 g m-diethynylbenzene, 0.5 g tri-o-tolylphosphine, 0.2 g palladium acetate, 0.1 g cuprous iodide and 300 mℓ triethylamine. After purging with nitrogen, the mixture was heated to 70°C and held for 56 hr. The mixture was filtered. The filtrate was stripped in vacuo and the residue taken up in toluene and washed with 10% hydrochloric acid followed by water. Stripping the solvent gave 22.33 g of oil A. This was washed with hexane to give 6.40 g of product. HPLC indicated it contained n=2, 4, 6, 8 compounds in the range 38, 40, 12, and 10%. The original filter cake was washed with water to remove amine salts and the residue dried in a vacuum oven to give 17.86 g of solid B essentially insoluble in methylene chloride indicating probable crosslinking.

M. Phase Transfer Oxidation of Acetylene Oligomers - Table VII

Run 712-8 is illustrative of the general procedure employed. An oligomer mixture, 6 g, consisting of n=2, 4, 6, and 8 compounds in the ratio 38, 40, 12, and 10% was dissolved in 300 mℓ methylene chloride. Potassium permanganate, 15 g, and dicyclohexyl-18-crown-6, 0.25 g, was added and the mixture refluxed 6 hr followed by stirring 66 hr at room temperature. Sulfuric acid, 100 mℓ, was added. Solid sodium bisulfite was added in small portions until the permanganate color disappeared and the manganese dioxide dissolved. A small amount of sodium bicarbonate soluble solids was removed by filtration. The filtrate was placed in a separatory funnel and washed with water, sodium bicarbonate, and water. The organic layer was dried over magnesium sulfate. The solvent was stripped to give 5.17 g of yellow solid. This

material was placed on a 125 mℓ volume of silica gel and eluted with hexane to give 0.50 g of colorless unreacted oligomers. The remainder of the material was eluted in several fractions using increasing amounts of methylene chloride and finally tetrahydrofuran. Each of the remaining fractions showed strong carbonyl absorption at 1675 cm^{-1}, but ^{13}C NMR indicated more acetylene carbon at 87-89 ppm than carbonyl carbon at 192 ppm in each fraction.

N. Preparation of Bromine-Terminated Benzil (712-60A)

This example is illustrative of the general procedure employed in the runs in Table IX. To a 1-ℓ Erlenmeyer flask was charged 25 g oligomer from Run 712-48 (avg. n=2.3), 300 mℓ 1,2-dichloroethane, 100 mℓ acetone, 50 mℓ acetic acid, and 50 mℓ water. The mixture was stirred vigorously with a magnetic stirrer, and 35 g potassium permanganate was added in a single portion. A mild warming to about 35°C occurred. The mixture was stirred for 20 hr. After addition of 100 mℓ of 10% sulfuric acid, solid sodium bisulfite was added slowly until the brown precipitate dissolved. A cold water bath was employed to maintain temperature below 35°C during this step. The reaction mixture was filtered through a bed of Celite® to remove insolubles. The filtrate was diluted with 1 ℓ of water and the organic layer separated. The aqueous portion was extracted with an additional 150 mℓ of dichloroethane. The combined organic layers were washed with water and saturated sodium bicarbonate solution before drying over magnesium sulfate. The solvent was stripped. Last traces of solvent were removed by melting the yellow solid under vacuum, 20.7 g, mp 60°C. HPLC indicated average n=2.2. NMR ($CDCl_3$) 7.0-8.3 δ broad multiplet.

O. Extraction of Lower Oligomers from Bromine-Terminated Benzil Oligomers (725-9C)

A mixture of oligomeric benzils (119.7 g) obtained from the permanganate oxidation (725-6) of the bromine terminated phenylacetylene oligomers was slurried with isopropanol (1 ℓ). The magnetically stirred mixture was warmed to reflux for 1 hr and allowed to cool to room temperature. Filtration and vacuum drying produced 97.9 g of product n=2.7. See Table XI for distribution.

P. Preparation of Bromine-Terminated Quinoxaline Oligomers (712-60B)

A 1-ℓ flask equipped with a condenser, magnetic stirrer, heating mantle, and Dean-Stark trap was charged with 20.0 g of bromine terminated benzil oligomer (n=2.2, 712-60B), 15.0 g o-phenylenediamine and 400 mℓ toluene. The mixture was brought to reflux. Water was no longer formed after about 1.5 hr but reflux was maintained for 3.5 hr. A total of 3.0 mℓ of water formed. This is consistent with n=2.2. The hot mixture was filtered to remove a small amount of dark insoluble material. The toluene was stripped in vacuo. Methanol, 300 mℓ, was added and the resulting solid pulverized in a blender. Filtration and vacuum drying at 50°C produced a tar solid, 18.9 g, mp 140-160°C. NMR ($CDCl_3$) δ 6.9-8.4 complex multiplet. Analysis: C, 63.34; H, 3.51; Br, 22.5; N, 7.93.

Q. Preparation of Bromine-Terminated Quinoxaline Oligomers (725-35)

Benzil oligomers from combined Runs 725-25, -28, and -29 (140 g) were extracted with isopropanol, vide supra, to yield 113.5 g. Because the HPLC was inoperative, n was estimated as 2.5 by bromine analysis--C, 55.23; H, 2.47; Br, 28.4. Unoxidized acetylene groups could not be detected by ^{13}C NMR. This material, 112.7 g, was charged to the apparatus employed in the previous example along with 650 mℓ toluene and 61.5 g o-phenylenediamine. Refluxing for 4.75 hr produced 17 mℓ water. After filtration, the toluene was stripped and the residue taken up in 200 mℓ dichloromethane. This solution was added dropwise to 1500 mℓ of methanol with vigorous stirring. The resulting precipitate was filtered and vacuum dried to give 108.9 g of produce, mp 140-160°C. Analysis: C, 66.04; H, 3.21; Br, 20.2, N, 8.93. The bromine analysis reflects n=2.8.

R. Preparation of Methylbutynol-Terminated Quinoxaline Oligomers (712-66)

A 1-ℓ flask equipped with a magnetic stirrer, heating mantle, condenser, thermocouple, nitrogen inlet-outlet and a rubber septum sample port

was charged with bromine-terminated quinoxaline oligomer from 712-60B, 18.8 g; bis-(triphenylphosphine) palladium dichloride, 0.1 g; triphenylphosphine, 0.25 g; 2-methyl-3-butyn-2-ol, 30 g; triethylamine, 300 mℓ; and cuprous iodide, 0.1 g; while purging with nitrogen. The mixture was refluxed for 22 hr. HPLC indicated no further reaction occurring. The mixture was cooled, filtered to remove amine salts, and stripped of solvent. The residue was taken up in 400 mℓ toluene and water washed (2 x 400 mℓ). Ethylene diamine, 20 g, was added and the solution warmed to 70°C for 30 min. After a thorough water washing, the solution was dried over magnesium sulfate. The toluene was stripped. The residue was dissolved in 100 mℓ dichloromethane. Dropwise addition to 1500 mℓ hexane produced an off-white colored precipitate which was filtered and dried to give 15.0 g, mp 110-140°C. NMR ($CDCl_3$) δ 1.5-1.6 (several overlapping singlets), 2.1(bs, exchanges with D_2O), 7.1-8.3 (complex multiplet). The ratio of the integrals was 6:1:10, respectively. This corresponds to n=2.

S. Preparation of Methylbutynol-Terminated Quinoxaline Oligomer (752-37)

A 2-ℓ flask equipped with a magnetic stirrer, heating mantle, condenser, thermocouple, nitrogen inlet-outlet, and a rubber septum sample port was charged with bromine-terminated quinoxaline oligomer from 752-35, 108 g; bis-(triphenylphosphine) palladium dichloride, 0.2 g; triphenylphosphine, 0.5 g; 2-methyl-3-butyn-2-ol, 200 mℓ; triethylamine, 1 ℓ; and 0.2 g cuprous iodide while purging with nitrogen. After 4.5 hr at reflux, an additional 0.2 g bis-(triphenylphosphine) palladium dichloride was added and reflux continued for another 24 hr as HPLC was not available to monitor reactions at this time. The mixture was filtered and the solvent stripped. The residue was taken up in toluene and washed with 5% HCl and then water until neutral washes were attained. The solution was dried over magnesium sulfate and the solvent stripped. The residue was taken up in dichloromethane passed through 1.5 kg of silica gel. Analysis indicated that the product still contained about 590 ppm Pd and 56 ppm Cu. A number of small samples were used to investigate the various metals removal schemes listed in Table XII. The remaining material was dissolved acetic acid, 500 mℓ, and precipitated by slow addition

to 3 ℓ of water with vigorous stirring. This precipitation was repeated once again from acetic acid and a further time from methanol. Atomic absorption analysis then indicated 45 ppm Pd and 9 ppm Cu. The NMR was similar to the previous sample except the ratio of the ingegrals was 6:1:15 corresponding to about n=3. Analysis: C,77.75; H, 5.51 ; N, 8.09 .

T. Preparation of ATQ Oligomer (712-70)

Methylbutynol-terminated quinoxaline oligomer from 712.66 was charged along with 300 mℓ toluene and 2 g of sodium hydroxide (pellets crushed) to a 500 mℓ flask equipped with a magnetic stirrer, heating mantle, Dean-Stark trap, and condenser. The mixture was refluxed for 2.5 hr periodically withdrawing the acetone toluene mixture from the trap. The hot solution was filtered. The solvent was stripped. The residue was dissolved in 50 mℓ dichloromethane and poured over 50 mℓ silica gel in a fritted glass filter funnel. Elution with 300 mℓ carbon tetrachloride was falled by stripping under vacuum to give 4.2 g light yellow solid, mp 90-115°C (prior softening at 70°C). NMR (CCl_4) δ 3.0 (overlapping singlets), 7.0-8.2 (complex multiplet). The ratio of acetylenic to aromatic protons was 1:10 corresponding to n=2.

U. Preparation of ATQ Oligomers (752-57)

Methylbutynol-terminated quinoxaline oligomer from 752-37, 78 g was charged along with 1 ℓ of toluene and 10 g of sodium hydroxide to a 2 ℓ flask equipped with a magnetic stirrer, heating mantle, and distillation head. Distillation of acetone-toluene mixture occurred at an overhead temperature of ~106°C. Over a period of 6 hr this increased to 110°C, the boiling point of pure toluene. The mixture was filtered hot and the toluene stripped. The residue was dissolved in 100 mℓ dichloromethane and poured onto 500 mℓ silica gel in a filter funnel. The silica gel was washed with carbon tetrachloride until no further product eluted. Stripping the solvent gave a summary material from which it was difficult to remove the last of the solvent. Redissolving in dichloromethane and precipitating in pentane produced a tan solid

which was filtered and dried under high vacuum for 4 d, 52.6 g, mp 120-155°C. NMR ($CDCl_3$) 2.9-3.0 (overlapping singlets), 7.0-8.2 (complex multiplet). The ratio of acetylene to aromatics was 1:15.7 corresponding to n=3.4. HPLC indicated n=3.3. Analysis: C, 82.17 ; H, 6.36 ; N, 8.72 .

V. Preparation of BPDS - General Procedure

A glass reaction vessel with a Fisher-Porter seal was charged with 7.5 g sulfonyldiphenol, 8.6 g cuprous oxide, 22.0 g of 2,4,6-collidine, and the desired amount of dibromobenzene. The reactor was placed in an explosion containment box and purged four times with nitrogen (50 psig). A 10 psig nitrogen pressure was put on the reactor. The temperature was raised to the desired level and maintained with a heating mantle while the mixture was magnetically stirred. After the desired reaction time, the mixture was cooled slightly, and the reaction mass transferred to a small distillation flask. Methylene chloride was used to aid in the transfer. Collidine and DBB were removed by vacuum distillation. The residue was dissolved in a minimum amount of methylene chloride. Carbon tetrachloride was added and the mixture filtered through a bed of Celite®. The filtrate was washed with 1:1 HCl, water, concentrated aqueous ammonia, and water. After drying over magnesium sulfate, the solvent was stripped under vacuum. The crude product was then analyzed by column chromatography or HPLC.

ETS:fli/dae
WPC(3388)

REFERENCES

1. R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, J. Polym. Sci, 15, 1081, (1977).

2. F. E. Arnold, F. L. Hedberg, and R. F. Kovar, Contemporary Topics in Polymer Science 2, Plenenum Press, 1978.

3. J. Casanova, Jr., M. Geisel, and R. N. Norris, Org. Prep. and Proc., 1, 81, (1969).

4. E. T. Sabourin, Preprints Div. Petr. Chem., 24, 233, (1979).

5. E. T. Sabourin, "Synthesis of Polymer Precursors and Exploratory Research Based on Acetylene Displacement Reaction," AFWAL-TR-80-4151, (1980).

6. D. R. Coulson, Chem. Commun., 1530, (1968).

7. P. Fitton and E. A. Rick, J. Organomet. Chem., 28, 287, (1971).

8. G. W. Parshall, J. Am. Chem. Soc., 96, 2360, (1974).

9. Private communication from R. F. Heck.

10. E. T. Sabourin and C. M. Selwitz, U.S. Patent 4,210,610.

11. Unpublished results at Gulf Research & Development Company.

12. C. B. Zeigler, Jr. and R. F. Heck, J. Org. Chem., 43, 2941, (1978).

13. K. Sonagshira, Y. Tohda, and N. Hazihara, Tet. Lett, 4467, (1975).

14. D. G. Lee and V. S. Chang, Synthesis, 462, (1978).

15. G. Rabillond and B. Sillion, J. Polym. Sci., 16, 2093, (1978).

16. L. Bassignam, A. Brandt, V. Caciagli, and L. Re, J. Org. Chem., 43, 4245, (1975).

17. G. Gebeyehu and E. McNelis, J. Org. Chem., 45, 4280, (1980).

18. N. S. Srinavasan and D. G. Lee, J. Org. Chem., 44, 1574, (1979).

19. J. J. Harrison and C. M. Selwitz, "Low Cost Routes to Acetylene Intermediates," AFML-TR-79-4183.

20. Private communication from F. L. Hedberg.

Table I

LIGAND SCREENING RUNS

Run No.	Substrate	Solvent	Ligand
712-6	A	triethylamine	triphenylphosphine
712-7	A	triethylamine	tri-o-tolylphosphine
712-13	A	dipropylamine	triphenylphosphine
712-58		diisopropylamine (40%) dimethyl sulfoxide (60%)	triphenylphosphine
712-90	A	diisopropylamine	ethyl diphenylphosphine
712-95	A	diisopropylamine	dicyclohexylphosphine
712-98	A	diproprylamine	ethyldiphenylphosphine
712-100	A	dipropylamine	diethylphenylphosphine
712-101	A	triethylamine	diethylphenylphosphine
712-103	B	triethylamine	diethylphenylphosphine
752-47	B	triethylamine	diethylphenylphosphine
752-48	B	triethylamine	pentafluorophenyl diphenyl-phosphine
752-49	B	triethylamine	benzyldiphenylphosphine
752-50	B	triethylamine	diisopropylphenylphosphonite
752-54	B	triethylamine	triphenylantimony
752-58	B	triethylamine	1,1-bis(diphenylphosphino)-ferrocene

ETS:fli
4/13/82
145-1100
3388-T

Table II

EFFECT OF TEMPERATURE AND SOLVENT ON REACTION RATE AND YIELD

Run No.	Catalyst System,[a] g Pd	P	CuI	DBB,[b] g	Solvent[c] (mℓ)	Temp., °C	Time, hr	Product, g
712-7	A,0.1	D,0.5	0.2	10	triethylamine (200)	90	5.0	Trace
-9	A,0.1	D,0.5	0.2	10	dipropylamine (200)	105	4.5	4.9[d]
-11	B,0.7[e]	D,0.5	0.2	100	dipropylamine (300)	112	29.0	33.9[f]
-16	B,0.6[e]	D,0.5	0.2	100	diisopropylamine (300)	87	13	[g]
-20	C,0.2	E,0.25	0.2	50	triethylamine (100) NMP (200)	100	23	28.6[f]
-23	C,0.2	E,0.25	0.2	50	diisopropylamine (100) NMP (200)	115	15	23.3[f]
-24	C,0.2	E,0.25	0.2	50	diisopropylamine (100) NMP (200)	100	29.5	24.2[h]
-27	C,0.2	E,0.25	0.2	50	diisopropylamine (100) DMAC (200)	100	14.5	11.6[h]
-28	C,0.2	E,0.25	0.2	50	diisopropylamine (100) DMSO (200)	94	9.5[i]	28.8[j]
-30	C,0.2	E,0.25	0.2	50	diisopropylamine (100) DMSO (200)	94	6[i]	30.2[j]
-34	C,0.2	E,0.25	0.2	50	diisopropylamine (100) DMSO (200)	75	8	15.7[j]
-112	A,0.2	D,0.5	0.2	50	triethylamine (100) chlorobenzene (200)	90	7	[g]
-113	C,0.2	E,0.25	0.2	50	triethylamine (100) chlorobenzene (200)	90	14	12.8[f]

---

a Pd components: A=palladium acetate, B=tetrakis-(triphenylphosphine) palladium, C=bis-(triphenylphosphine) palladium dichloride; Phosphine components: D=tri-o-tolylphosphine, E=triphenylphosphine.

b m-dibromobenzene.

c NMP=N-methylpyrrolidinone; DMAC=dimethylacetamide; DMSO=dimethylsulfoxide.

d Isolated by filtration and water wash-insoluble in methylene chloride.

e Added incrementally.

f Unreacted DBB distilled from crude product to give product as residue.

g GLC shows very slow reaction. Product not isolated.

h Methylene chloride solution of crude product precipitated in methanol.

i GLC shows all DBB reacted.

j Total reaction mixture poured into water, filtered, and dried.

ETS:fli
4/13/82
145-1100
3388-T

Table III

BROMINE-TERMINATED ARYLACETYLENE OLIGOMERS - PREPARATIVE RUNS

Run No.	Catalyst[a]	Phosphine[b]	CuI, g	DBB,[c] g	DIA,[c] ml	DMSO,[c] ml	$T_{T,h}$[d]	$T_{R,h}$[d]	Product, g
712-45	0.2	0.25	0.2	50	100	200	5	5	28.9 (12)[e]
-47	0.4[f]	0.25	0.2	50	100	200	5	5	24.3
-48	0.2	0.25	0.2	50	100	200	5	5	24.1
-49	0.4[f]	0.25	0.2	50	100	200	10	10	25.0 (39)
-50	0.2	0.25	0.2	50	100	200	5	4.5	22.6
-51	0.4[f]	0.25	0.2	50	100	200	11	9	23.3
-67	0.4[f]	0.25	0.2	50	100	200	24	6	29.6 (100)[e]
-69	0.4	0.25	0.2	50	100	200	24	6	29.6 (100)[e]
-72	0.4	0.25	0.2	50	100	200	7	--	26.9
-74	0.4	0.25	0.2	50	100	200	7	4	26.7 (32)[e]
-75	0.4	0.25	0.2	50	100	200	6.5	4	29.8 (32)[e]
-80	0.2	0.25	0	50	100	200	4	--	Traces
-114	0.4	0.5	0.2	50	100	200	3.25	3	25.8
-115	0.4	0.5	0.2	50	100	200	3	2.5	25.2
-116	0.8	1.0	0.2	100	200	400	11	--	12.5[g]
752-2	0.4	0.5	0.2	50	100	200	2.25	2.25	25.3
-3	0.4	0.5	0.2	50	100	200	5.5	2	33.4
-4	0.4	0.5	0.2	50	100	200	4.5	3	30.0
-5	0.8	1.0	0.4	100	200	400	6	4	61.5
-10	0.8	1.0	0.4	50	200	400	4	2	28.2 (40)[e]
-13	0.8	1.0	0.4	100	200	400	3	3	56.4
-19	0.8	1.0	0.4	100	200	400	5	5	61.2
-20	0.8	1.0	0.4	100	200	400	5	5	59.4
-21	0.8	1.0	0.4	100	200	400	5	5	60.7
-22	0.8	1.0	0.4	100	200	400	5	5	60.3

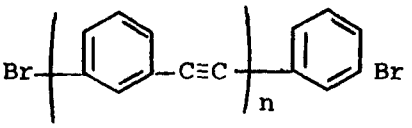
---

a bis(triphenylphosphine) palladium dichloride
b triphenylphosphine
c DBB = dibromobenzene; DIA = diisopropylamine; DMSO = dimethylsulfoxide
d T_T = total reaction time; T_D = time of disappearance of DBB by GLC
e Percent insolubles in product-probably crosslinked polymer.
f Add in 0.2 g increments.
g Because of large amount of DBB unreacted, considerable product may have been lost during filtration.

ETS:WPC
4/13/82
145-1100
3388-T

Table IV

OLIGOMER DISTRIBUTION[a]



Run No.	n = 1	2	3	4	5+	Average n
712-20	51.2	29.0	11.4	4.2	0.5	1.6
-23	61.4	27.7	5.2	4.1	--	1.5
-28	26.8	28.1	20.8	13.8	10.6	2.5
-30	21.8	27.0	24.0	16.8	10.3	2.7 (2.9)[b]
-45	25.6	28.7	22.6	14.5	8.6	2.2
-47	20.1	28.7	24.7	16.2	10.3	2.4
-48	22.1	30.4	25.0	14.6	8.0	2.3
-49	14.1	27.1	27.5	20.6	10.7	2.6
-50	15.2	30.0	27.2	18.4	10.3	2.5
-51	11.9	26.6	25.8	21.0	14.7	2.7
-114	18.0	30.9	28.1	18.8	4.3	2.6
-115	10.8	29.9	24.6	20.7	14.0	3.0
752-1	11.3	22.2	26.9	21.7	17.8	3.1
-2	19.6	27.6	25.6	18.5	8.7	2.7
-3	14.7	22.6	25.9	21.1	15.7	3.0
-4	15.2	23.1	27.1	21.9	12.7	2.9
-5	16.2	24.5	27.1	21.1	11.0	2.9
-10	10.8	19.0	25.1	24.2	20.9	3.2

---

a Determined by HPLC.
b Determined by bromine analysis.

ETS:llm
4/13/82
145-1100
(3388-T)

Table V

EXTRACTION OF LOWER ACETYLENE OLIGOMERS

Run No.	752-2		752-7	
Initial Weight, g	25.3		124.9	
Final Weight, g	15.4		99.9	
Hexane, ml	500		1000	
Distribution	Initial	Final	Initial	Final
M				
1	19.6	1.2	15.2	3.1
2	27.6	24.1	23.1	20.8
3	25.6	29.5	27.1	31.6
4	18.5	25.5	21.9	27.7
5+	8.7	19.7	12.7	16.7
Avg.	2.7	3.4	2.9	3.4

ETS:llm
4/13/82
145-1100
(3388-T)

Table VI

REACTION OF BROMOPHENYLACETYLENE WITH LOWER BROMINE TERMINATED PHENYLACETYLENE OLIGOMERS[a]

Run No.	Oligomer, g	Bromophenyl-acetylene, g	Addition Time, hr	Product, g		Distribution of Soluble Portion				
				Total	Insoluble	n=1	2	3	4	5+
Starting Material						30.0	56.9	10.1	3.0	--
752-40	10	10	2	15.89	9.48	4.0	21.0	30.2	27.4	17.3
752-41	10	20	4	21.38	17.14	2.8	9.4	19.9	31.8	36.1

a Reaction Conditions: A mixture of oligomer in 100 ml diisopropylamine and 200 ml DMSO containing 0.4 g bis-triphenylphosphine palladium chloride and 0.2 g cuprous iodide heated to reflux under nitrogen. Bromophenylacetylene added dropwise from addition funnel. Reaction maintained at temperature 30 min after addition complete.

ETS:llm
4/13/82
145-1100
(3388-T)

Table VII

PHASE TRANSFER OXIDATION OF ACETYLENIC OLIGOMERS

Run No.	Oligomer Source	Oligomer g	$KMnO_4$, g	Solvent (ml)	Other Reagents, g	Temp, °C	Time, hr	Product, g
712-15	712-8C	6.0	15	dichloromethane (300)	crown[a] (0.25)	ambient	66	5.2[b]
712-22A	712-11B	12.6	10	dichloromethane (500)	crown[a] (0.3)	40	20	No Reaction
712-22B	712-22A	12.6	5	1,2-dichloroethane (300)	crown[a] (0.2)	83	22	Trace[c]
712-31	712-28	5.0	10	dichloromethane (200)	Adogen-464 (1.5) acetic acid (10)	40	4	5.9[d]
712-32	712-28	5.0	10	dichloromethane (200)	crown[a] (0.25) acetic acid (10)	40	20	3.7[b]
712-36	712-28	5.0	5	dichloromethane (200)	crown[a] (0.25) acetic acid (10)	40	20	4.4[b]
712-37	712-28	5.0	4	dichloromethane (200)	crown[a] (0.25) acetic acid (10)	40	20	5.3[b]
712-38	712-30	5.0	5	1,2-dichloroethane (200)	crown[a] (0.25)	83	4	5.0[b]

a Dicyclohexyl-18-crown-6
b Not all acetylene groups oxidized in each molecule.
c IR shows weak carbonyl band.
d Contaminated with Adogen-464.

ETS:llm
4/13/82
145-1100
(3388-T)

Table VIII

OXIDATION OF ACETYLENE OLIGOMERS IN HOMOGENEOUS SYSTEMS

Run No.	Oligomer Source	Oligomer g	$KMnO_4$, g	Solvent[a]	Temperature	Time, hr	Product, g
712-41	712-30	5.0	5	tetrahydrofuran	ambient[b]	20	4.7[c]
712-52	712-30	5.0	15	dimethylacetamide	ambient[d]	20	1.4 (82)[e]
712-53	712-30	5.0	15	" "	5[f]	20	1.5 (75)[e]
712-54	712-30	5.0	15	" "	35 (max)	20	1.3 (88)[e]
712-55	712-30	5.0	5	" "	35 (max)	20	2.5 (57)[e]
712-64	712-30	5.0	7	acetonitrile	ambient	20	1.4 (57)[e]

a Acetic acid, 10 g, also present. 200 ml solvent used.
b THF reacts with $KMnO_4$, complicating reaction.
c Partial oxidation.
d Strong exotherm initially.
e Parentheses indicate amount product which is n=1.
f Initial temperature allowed to rise slowly to ambient.
g Added in 3g increments at 0.5 hr interval.

ETS:llm
4/13/82
145-1100
(3388-T)

Table IX

OXIDATION OF ACETYLENE OLIGOMERS IN MIXED SOLVENTS[a]

Run No.	Oligomer Source	Oligomer g	$KMnO_4$, g	Solvent Composition, ml CH_2Cl_2	$(CH_3)_2CO$	CH_3COOH	H_2O	Other Reagents, g	Product, g
712-22C	712-22B	13.4	10	200	300	--	100	$NaHCO_3$, 0.5; $MgSO_4$, 5.0	7.8
712-25	712-20	28.6	20	--	500	--	200	$NaHCO_3$, 1.0; $MgSO_4$, 6.0	17.9[b]
712-40	712-30	5.0	5	300	300	50	100	--	4.6[b]
712-44	C	28.0	20	300	100	50	50	--	15.7
712-56	712-45	25.0	25	300	100	50	50	--	17.8
712-59	712-47	25.0	35	300	100	50	50	--	20.2
712-60	712-48	25.0	35	300[d]	100	50	50	--	20.7
712-68		50.0	70	600	200	100	100	--	34.1
712-77	712-74	26.5	37.5	200	100	50	50	--	10.5
712-87	712-75 -76,-78	80.5	100	1100	240	150	100	--	b,c
712-91	--	63.6	80	640	240	120	80	--	b,c
712-93	e	e	80	640	240	120	80	--	48.9
752-6	712-23	176.9	300	2400	800	400	400		f
752-68	f	f	50	2400	800	400	400		101.7
752-14	752-1,10	80.3	125	90.0	300	150	150		43.5
752-25	752.23	117.4	183	1300	450	450	200		47.4
752-28	752-26	115.8	183	1300	450	200	200		61.8
752-29	752-14	43.5	75	900	300	150	150		31.0

---

a All runs at ambient temperature for 20 hr.
b Partial oxidation.
c Partial oxidation products from Runs 712-32, 33, 36, 37, 38, 40, 41.
d 1,2-dichloroethane substituted for dichloromethane.
e Partially oxidized products from 87 and 91 not isolated but combined and recharged to 712-93.
f Incomplete oxidation, rerun in 752-6B.

ETS:llm
4/13/82
145-1100
(3388-T)

Table X

EFFECT OF OXIDATION ON THE VALUE OF n

	752-6		752-28	
Run No.	Acetylene	Benzil	Acetylene	Benzil
1	15.4	22.1	3.1	8.9
2	26.1	33.9	20.8	28.7
3	25.2	30.3	31.6	34.5
4	19.5	13.0	27.7	20.8
5+	13.7	1.8	16.7	7.0
Avg.	2.9	2.4	3.4	2.9

ETS:llm
4/13/82
145-1100
(3388-T)

Table XI

EXTRACTION OF LOWER BENZIL OLIGOMERS

Run No.	752-9A		752-9C	
Initial Weight, g	20.0		119.7	
Final Weight, g	13.6		97.9	
Isopropanol, ml				
Distribution	Initial	Final	Initial	Final
1	18.6	12.4	22.1	10.8
2	24.6	28.0	33.9	33.8
3	29.4	28.7	30.3	33.7
4	16.6	22.8	13.0	18.1
5+	4.8	9.2	1.8	3.6
Avg.	2.4	2.9	2.4	2.7

ETS:llm
4/13/82
145-1100
(3388-T)

Table XII

METALS REMOVAL

Trial No.	Treatment	Pd, ppm	Cu, ppm
	none	590	56
A	ethylene diamine (g/g) reflux in CH_2Cl_2 30 min	340	54
B	30% H_2O_2 (equal weight); reflux in $CHCl_2$	660	59
C	CH_2Cl_2 solution washed with aq. NH_4Cl (2.5 g/g), ethylene diamine (g/g) added reflux 30 min water wash until neutral	160	66
D	CH_2Cl_2 solution washed with aq NH_4CL (2.5 g/g), diethylene triamine (g/g) added reflux 30 min water wash until neutral	160	39
E	25-fold sample treated two times as in D	240	44
F	6 NHCl (40 ml/g), neutralized with NH_4OH, extract with CH_2Cl_2, water wash	150	68
G	Dissolve in acetic acid (20 ml/g) add slowly to water (200 ml), filter, wash with conc. NH_4OH then water	130	19
H	Repeat G on 25-fold scale (using recovered material from E)	84	19
I	Material recovered from filtrate of H	240	52
J	Dissolve in acetic acid (20 ml/g), add slowly to conc. NH_4OH, filter and wash until neutral	81	45
K	Dissolve in hot methanol (20 ml/g), cool to room temperature, filter, add filtrate to water, filter precipitate, and dry	67	5
L	Dissolve in methanol containing diethylene triamine (g/g), reflux 30 min, work up as in K	58	14

ETS:llm
4/13/82
145-1100
(3388-T)

Table XIII

EFFECT OF TEMPERATURE AND PRESSURE[a] ON BPDS PREPARATION

Run No.	DBB/SDP/Cu_2O/TMP	Temp, °C	Time hr	Crude Prod., G	wt% BPDS HPLC[c]	wt% BPDS Column[d]	Ratio BPDS/Olig. HPLC	Ratio BPDS/Olig. Column	%Yield BPDS + Olig. Column[e]
712-83[b]	6 1 2 6	170	44	12.9	60.4	60.4	1.8	1.9	78
712-84	6 1 2 6	190	21	16.5	45.4	41.8	1.8	2.3	65(79)
712-86	6 1 2 6	190	7	8.9	45.1	37.3	3.7	3.1	27(53)
712-88	6 1 2 6	210	6.5	12.2	54.91	50.0	1.5	1.4	70(82)
712-89	4 1 2 6	190	16	7.0	nd	40.0	nd	1.7	19(41)

---

a An initial 10 psig pressure of nitrogen employed. Pressure in the sealed vessel rose to between 20 and 30 psig in the runs.

b Control run at atmospheric pressure under nitrogen.

c Normal phase nitrile column, isocratic elution with 60% hexane-40% methylene chloride containing 3% isopropanol, 1 ml/min flow, 30°C.

d Approximately 0.5 g crude product on a 25 ml column of silica gel in a 100 ml burette. Sequential elution with CCl_4; 2:1-CCl_4:CH_2Cl_2; 1:10-CCl_4:CH_2Cl_2; 9:1-CH_2Cl_2:$(C_2H_5)_2O$ to give DBB; BPDS; oligomer 1; oligomer 2; higher oligomers + half-product, respectively.

e Parenthesis indicates total yield of half-product is included.

ETS:llm
4/13/82
145-1100
(3388-T)